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THE DEVELOPMENT OF A NEW IRON CATALYST FOR THE DIRECT LIQUEFACTION OF COAL

Robert BACAUD*, Michelle BESSON* and G rard DJEGA-MARIADASSOU†

* C.N.R.S., Institut de Recherches sur la Catalyse
2, Av. Albert Einstein, 69626 Villeurbanne cedex, France

† Laboratoire de R activit  de Surface et Structure
Universit  P & M Curie, 75232 Paris cedex 05, France

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INTRODUCTION

The present paper is a synthesis of the research conducted in a program for the development of iron based catalysts, as a part of a project supported by French government and E. C. between 1980 and 1990. The objective was to provide an evaluation of the feasibility of producing substitute natural gas and liquid transportation fuels, through liquefaction of coal. The development of liquefaction catalysts was performed at laboratory scale in our Institute and the testing of dispersed iron based catalysts was conducted in a 50 kg/d facility at CERCHAR (Charbonnages de France).

The eventual influence of a catalyst upon coal dissolution is a-priori questionable. However, considerable experimental evidence has been accumulated that demonstrates the ability of hydrogenation catalysts to increase the production of soluble compounds from coal at relatively low temperature. This conversion coincides with some hydrogenation which is also enhanced by catalysts. Although low temperature liquefaction cannot generate radical species through homolytic bond cleavage, some coal macerals - especially inertinite - contain significant concentration of free fossil radicals. The initial dissolution process makes these species accessible for further reaction and condensation. The role of catalysts in these conditions is to provide a source of active hydrogen in order to cap these radical species and to avoid retrogressive reactions.

At higher temperature, the rate of radical production increases, as well as the rate of the concomitant reactions of homolytic rupture and condensation, respectively responsible for the formation of gases and insoluble products. A fast stabilization of radical species through hydrogenation contributes to an improvement of selectivity for the production of distillate by reducing the formation of gases and solid residues. A hydrogenation catalyst will prove useful for process control at increased severity but it must demonstrate its usefulness, since it operates in a highly competitive medium where several species can assume some role in hydrogen transfer mechanisms; the more serious competitor for any additional catalyst is the pyrite contained in coals, activity of which is undeniable.

The choice of a catalyst destined to be used in the form of a flowing disposable solid is dictated by the difficulty, even the impossibility, to recover a catalytic substance mixed with unconverted coal and mineral matter. This choice implies a set of requirements must be fulfilled by the catalytic material:

- As an unrecovered reactant, its cost must be low. This primary consideration has considerably limited the range of investigated candidates.
- The solid catalyst is flowing along with the reactants. It is therefore necessary to reduce the amount of displaced substance, both for avoiding the

transport of useless material and for limiting the problems associated with sedimentation and abrasion of reactor and equipments.

- A low catalyst-to-coal ratio imposed by process optimization means the active phase must exhibit a high intrinsic activity.

We decided to develop a synthetic method for the production of a catalyst, considered as the only way of ensuring a proper control of the properties, choosing iron as the cheapest raw material. Among transition metals sulfides, iron is not extremely active (1); its low intrinsic activity must be compensated by a high dispersion. The next step of our program consisted in an investigation of the methods of preparation of highly dispersed iron oxides, considered as precursors for the in-situ generation of iron sulfide during coal liquefaction.

PRODUCING THE CATALYST PRECURSOR

The methods of preparation of heterogeneous catalysts attempt to increase the surface area of the solids. The easiest way consists in producing a porous substance or in supporting the active phase on a porous support. Our first approach consisted in comparing the properties of catalysts obtained by means of deposition of iron compounds on various high surface area supports.

Table I. Characteristics and liquefaction behavior of supported iron oxides

Support	BET S.m ² .g ⁻¹	Pore radius nm	H increment $\Sigma^{(a)}$
Carbon black	115	Non porous	0
SiO ₂	100	15	0
Al ₂ O ₃	100	20	0
SiO ₂ -Al ₂ O ₃	600	3	8

(a): relative increment of hydrogen incorporation in coal products as compared to a non catalytic experiment.

Table I clearly illustrates the fact that an active phase, well dispersed on the porous structure of a high surface support, is completely inactive for hydrogen transfer reactions. From these results, it was evident that our attempts should be oriented towards the preparation of high external surface area iron solids. We prepared pure iron oxides by precipitation from a nitrate solution with ammonia and we tried to increase the surface by introducing small amounts of various textural promoters, coprecipitated along with iron hydroxide. Only alumina provided some positive effect upon the surface area and liquefaction activity of these solids. A change in the drying process produced a major impact than the introduction of textural promoter as illustrated by table II.

It appeared that hydrogen transfer activity in coal liquefaction is not directly correlated with surface area of the active phase but with the changes in morphology of the particles induced by spray drying.

Ours investigations turned towards the methods of preparation of highly dispersed, non porous solids. A rather simple method consisting in the hydrolysis of volatile compounds in a hydrogen-oxygen flame, currently used for commercial scale production of aerosol oxides of aluminium, silicium and titanium, had been recently adapted to the elaboration of iron oxide (2). Spherical particles are obtained with narrow particle size distribution. The mean particle size can be as small as 10 nm and can be varied through control

of the respective flows of metallic compound vapors and of the gases in the torch. The properties and liquefaction behavior of these catalysts are presented in Table II.

Table II. Characteristics and liquefaction behavior.
Unsupported iron oxides

Catalysts	Drying	BET S. $\text{m}^2 \cdot \text{g}^{-1}$	H increment % ^(a)
Precipitated oxides			
Fe ₂ O ₃	Oven	150	10
Fe ₂ O ₃	Spray	160	15
Fe ₂ O ₃ -Al ₂ O ₃ 10%	Oven	270	4
Fe ₂ O ₃ -Al ₂ O ₃ 10%	Spray	200	18
Aerosol iron oxides			
Lab. scale 1		40	18
Lab. scale 2		32	18
Pilot		24	12

(a): Relative increment of hydrogen incorporation in coal products as compared to a non catalytic experiment.

SULFIDATION OF IRON OXIDE

The oxides obtained in a convenient divided state are the precursors of the actual catalytic phase, which results from the interaction of iron oxide with the reacting medium during liquefaction. Owing to the sulfur content of the majority of coals, the partial pressure of hydrogen sulfide can be expected to range around 0.5-2 % in the gas phase during liquefaction. During the early stage of liquefaction, before hydrodesulfurization of coal takes place, the catalyst precursor will be in contact with a highly reducing medium with low initial concentration of hydrogen sulfide; the release of sulfur from coal progressively modifies the composition of the gas phase.

Preliminary experiments revealed that iron oxide is easily transformed into a pyrrhotite Fe_{0.91}S at moderate temperature under hydrogen sulfide partial pressure ranging from 0.2 to 1% in hydrogen (3). Although sulfidation produces a severe decrease of surface area, the resulting phase is active in the reaction of tetralin dehydrogenation in the presence of hydrogen sulfide (Table III).

Table III. Characterization and catalytic activity of iron sulfides generated by gas phase sulfidation of an unsupported iron oxide (BET S. = $24 \text{m}^2 \cdot \text{g}^{-1}$)

Treatment	Phases	BET S. $\text{m}^2 \cdot \text{g}^{-1}$	Activity $\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}(\text{a})$
1 - H ₂ S	Fe _{0.91} S	3	$4 \cdot 10^{-8}$
2 - H ₂	Fe _{0.995} S	3	$0.3 \cdot 10^{-8}$
1 - H ₂	Fe	2	$10 \cdot 10^{-8}$
2 - H ₂ S	Fe _{0.995} S	0.1	$0.1 \cdot 10^{-8}$

(a) Catalytic activity in dehydrogenation of tetralin at 600 K, 0.1 MPa H₂

A reduction of this sulfide under hydrogen generates a considerably less active phase, identified as Fe_{0.995}S. A preliminary reduction of iron oxide under hydrogen produces a very active metallic phase. Partial sulfidation of metallic iron completely inhibits its activity. The production of Fe_{0.995}S by

sulfidation of metallic iron by hydrogen sulfide is very progressive and gives rise to a drastic sintering (4).

This study was completed by an examination of the influence of the protocol of sulfidation and introduction of the catalyst in the reacting medium during coal liquefaction, in the presence of a hydrogen-donor solvent (tetralin). We compared the ability of catalysts to rehydrogenate the solvent, after different sulfidation protocols described below.

- In-situ sulfidation: the catalyst precursor is introduced into the reactor along with the reactants and sulfur, then heated up to the reaction temperature.

- Pre-sulfidation: either in the gas phase, by a mixture containing 1 % hydrogen sulfide in hydrogen, or in suspension in tetralin under 1 % H_2S in H_2 at 15 MPa total pressure.

- Flash-sulfidation: the precursor is introduced under pressure (15 MPa) in the autoclave containing the reacting medium (coal, solvent, H_2S and H_2) at reaction temperature.

As evidenced in table IV, only catalysts pre-sulfided in gaseous H_2S or in-situ sulfided are active for solvent hydrogenation. The drastic reduction of activity caused by a pre-sulfidation in tetralin suggests that coal itself must interfere with the process of generation of the active phase from iron oxide.

Table IV. Influence of sulfidation protocol upon solvent hydrogenation during coal liquefaction (tetralin 673 K, 1% H_2S)

Protocol	% Solvent dehydrogenated
In-situ	2
Gas phase pre-sulfidation	3
Liquid phase pre-sulfidation	13
Flash sulfidation	13
No catalyst	13

A systematic electron microscope examination, associated with X-ray emission micro-analysis, revealed an agglomeration of sulfide particles when the precursor was sulfided in the absence of coal; the surface of the grains was covered with an opaque, thick layer of coke probably resulting from cracking of tetraline (5). On the contrary, samples originating from in-situ sulfidation, in the presence of coal, showed that the sulfided particles preserved the particle shape of the precursor. A smooth carbonaceous deposit was evidenced at the surface of the particles. This layer, as opposed to the dense coke formed in tetralin, preserved the hydrogenation activity (6). It may result from adsorption of dissolved coal products which prevent particles agglomeration.

EVALUATION OF CATALYSTS IN COAL LIQUEFACTION

Using a disposable catalyst prescribes low catalyst-to-coal ratio. An evaluation of catalysts for coal liquefaction must include determining the minimum loading required for a given level of conversion. In this part of our project, we chose conditions of high severity liquefaction, i.e. high temperature and a non-donor solvent. Coke buildup occurs in these conditions for non catalytic experiments. As a tool for catalysts evaluation, we determined the minimum amount of catalyst required for unperturbed reactor operation during 1 hour runs. This arbitrary criterion, designed as "critical catalyst loading", does not attempt to define an absolute value but is

indicative of the relative performances of distinct catalysts. Some of the catalysts included in table V are representative of the improvements we obtained in the synthesis of iron oxide. The effect of increasing external surface area is evidenced, as well as the doping effect produced by incorporation of minor amount of molybdenum.

Table V. Critical catalyst loading

Catalyst	Weight % vs coal
Red mud	2.2
Fe_2O_3 , $18 \text{ m}^2 \cdot \text{g}^{-1}$	0.7
Fe_2O_3 , $71 \text{ m}^2 \cdot \text{g}^{-1}$	0.4
Fe_2O_3 , 2.8 % MoO_3	0.2
Fe_2O_3 , 18 % MoO_3	0.2

The influence of catalyst loading on oil yield is presented in Fig. 1 for some representative catalysts. The change in oil production is not proportional to the catalyst content and a twofold increase of catalyst percentage only causes oil yield to vary from about 40% to 50%.

The relation between the amount of hydrogen incorporated into the final liquid coal products and the percentage of catalyst is described in Fig. 2. It must be specified that the values correspond to a net H_2 incorporation and that the contribution of hydrogen to the formation of light gases from the organic matter of coal has been subtracted; increasing the amount of red mud for example, enhances hydrogen consumption, but this additional H_2 is mainly utilized for the production of gases. On the contrary, the net hydrogen incorporation augments with increasing the amount of iron oxide based catalysts, and it reaches higher levels than with Ni-Mo. As indicated above, oil production varies little with the nature and with the percentage of catalyst. Consequently, the hydrogen content of the oils produced in distinct catalytic conditions - and therefore oil quality - must vary accordingly. This is reflected by the percentage of H_2 incorporated into oils or into (oils + asphaltenes) reported in table VI.

Table VI. Weight % H_2 incorporated into oils or asphaltenes

Catalyst (1.5% vs. coal)	H_{oil}	$\text{H}_{\text{oil+asphalt}}$
Fe_2O_3 , $71 \text{ m}^2 \cdot \text{g}^{-1}$	4.44	3.49
Fe_2O_3 , 2.8% MoO_3	4.38	4.05
Ni-Mo/ Al_2O_3	3.48	2.60
Red mud	3.0	2.15

From a linear regression of the rate of hydrogen consumption versus the pressure decrease, an initial rate of H_2 incorporation could be deduced. The results are presented in Fig. 3. This apparent initial rate reflects the activity of the fresh catalyst. Initial activity for Ni-Mo is superior to that of pure iron oxide, although the products obtained with the former are less hydrogenated; the same is observed concerning the hydrogenation of the solvent (Fig. 4): iron based catalysts exhibit a higher activity than Ni-Mo. Although supported Ni-Mo is intrinsically a better catalyst than iron sulfide (as evidenced by its higher initial activity), its exposed active surface declines rapidly, due to the plugging of the porous structure by carbonaceous deposits. On the contrary, the surface of unsupported iron sulfides is

affected to a less extent by this phenomena, and consequently their activity can maintain at a convenient level.

CONCLUSION

As part of a program for the production of fluid fuels through coal liquefaction, we investigated the pertinent basis for the elaboration of catalytic materials. Considering the requirements imposed by the specific conditions of use of disposable catalysts in coal liquefaction, we decided to prepare synthetic iron based solids. The prominent results of this program are summarized below:

- Catalytic activity relies upon the external surface area. Porous solids that exhibit a high surface are inactive, as compared to non porous ones.
- Nanometer-sized iron oxides (aerosol) can be produced through vapor phase hydrolysis of volatile compounds in a hydrogen-oxygen flame. They exhibit uniform spherical shape particles whose diameter can be as low as 10 nm.
- Sulfidation of these precursors generates a pyrrhotite at moderate temperature. A previous reduction of iron oxide to the metallic state must be avoided, since further sulfidation is considerably more difficult.
- Coal provides a support effect during sulfidation and prevents, up to some extent, the agglomeration of catalyst particles.
- The performances of aerosol iron oxides in coal liquefaction largely exceed those of red mud and compare favourably with commercial supported Ni-Mo catalysts. They can be improved by incorporation of minor amounts of molybdenum.
- Critical catalyst loading, indicative of the minimum catalyst-to-coal ratio compatible with reactor operability, suggests that the proposed catalysts can be used at concentration levels as low as 0.2% vs coal.

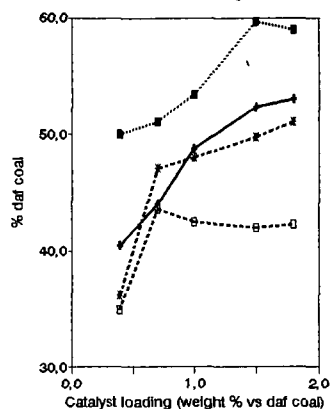
ACKNOWLEDGMENTS

H. Charcosset, presently retired, initiated and gave the impulse to this program. His role, as a group leader of the French laboratories included in this project, has been decisive. We wish, by means of this paper, to express our gratitude for his essential contribution.

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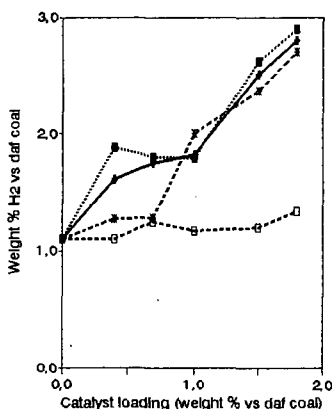
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Fig. 1: Oil yield
as a function of catalyst loading



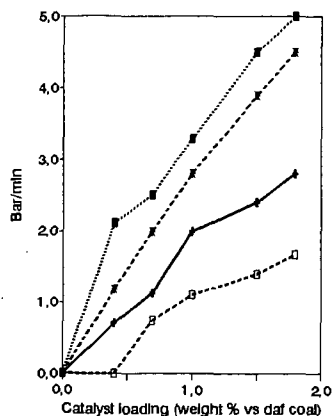
---■--- Fe-Mo —●— Fe - - -▲- - - Ni-Mo ···◇··· Redmud

Fig. 2: hydrogen incorporation
in coal liquids



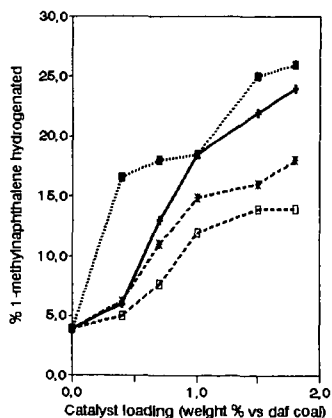
---■--- Fe-Mo —●— Fe - - -▲- - - Ni-Mo ···◇··· Redmud

Fig. 3: Initial rate of H₂ uptake
Liquefaction 723K, non donor solvent



---■--- Fe-Mo —●— Fe - - -▲- - - Ni-Mo ···◇··· Redmud

Fig. 4: Solvent hydrogenation
Liquefaction 723K, 1 hr residence time



---■--- Fe-Mo —●— Fe - - -▲- - - Ni-Mo ···◇··· Redmud